AN ASYMPTOTIC EXPRESSION FOR THE CRITICAL-REGION "BIRD'S BEAK" ISOTHERM AND ADJACENT ISOTHERMS ON THE VAPOR-LIQUID PHASE DIAGRAM OF A SIMPLE BINARY MIXTURE*

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ABSTRACT

For a binary mixture of a dilute nonvolatile solute in a volatile solvent, an asymptotic expression is derived for isothermal dew-bubble curves in the region just above the solvent critical point. The expression depends only on the solvent coexistence properties and the initial slopes of the continuous critical locus, with no adjustable parameters. It clarifies the mathematical behavior of these curves and shows why, for this situation, classical critical exponents can be used with relatively small error. For supercritical extraction applications, the expression does not apply to solutes with large, complex molecules, since the critical locus with carbon dioxide is usually discontinuous, but it should apply to carbon dioxide + cosolvent mixtures. The formula is in good quantitative agreement with experiment for three simple nonpolar mixtures and for carbon dioxide + acetone, but shows only qualitative agreement for carbon dioxide + ethanol.

I. INTRODUCTION

Thermodynamic behavior and phase equilibria of fluids and fluid mixtures in the near-critical region are characterized by critical exponents, which differ in value from classical exponents that result from standard equations of state [1]. For purposes of accurate thermodynamic correlations, usually the most important critical exponent is β. If T is the temperature of coexisting liquid and vapor states of a pure fluid with densities ρ_ℓ and ρ_v respectively, then:

$$(\rho_\ell - \rho_v) / \rho_c = 2C_1 \left[(T_c - T) / T_c \right]^\beta = 2C_1 (-t)^\beta \tag{1}$$

where the subscript c denotes critical value and C_1 is a constant. Classically $\beta = 0.5$, but according to the modern theory of critical phenomena, $\beta = 0.325$ within the region very near the critical point. For some purposes [2], an "effective" value of $\beta = 0.355$ makes Eq. (1) a useful (but approximate) fitting function over a wider range, typically $-0.1 < t < 0$.

At present, even in the critical region, vapor-liquid equilibria of mixtures are most frequently modeled by classical equations of state, including commonly used cubic equations such as the Redlich-Kwong [3] and Peng-Robinson [4] equations. Some nonclassical models with theoretical or effective critical exponents are available, such as the Leung-Griffiths model [5] as modified by Rainwater and Moldover [2, 6] and related models that incorporate crossover functions to connect the critical and noncritical regions [7-11]. Such models are currently used in a correlative rather than a predictive mode, since in general they require the critical locus as input as well as a number of adjustable parameters that can be determined only when extensive experimental data are available. Also to date, they have been used only in a limited degree for multicomponent mixtures [12-14], caloric properties [9,15], and mixtures with discontinuous critical loci [16], subjects which are generally easily studied by means of classical equations of state. A question that then arises is how much error is caused by the use of an equation that leads to (incorrect) classical critical exponents. The answer, of course, depends on the thermophysical property that is being studied. One general observation is that proper exponents appear to be more important for densities than for the pressure-temperature-composition phase boundary.

For the P-T-x-y phase boundary surface without regard to densities, the problems with

classical equations of state are less evident. Commonly used phase equilibrium algorithms can fail to converge in the critical region, but this is a deficiency of the algorithm rather than the equation of state itself. For isotherms just above the critical temperature of the more volatile component, as seen in the numerous Peng-Robinson correlations of Knapp et. al. [17], and elsewhere, the classical equation of state frequently appears to agree well with experimental data all the way to the critical point. One conclusion of the present work is that it is this type of diagram, and this region of that diagram, in which the errors introduced by classical critical exponents are not of great importance, in contrast to other diagrams and regions of the P-T-x-y diagram.

Our primary result is a simple asymptotic formula for isothermal dew-bubble curves at temperatures just above the critical temperature of the volatile component, and which thus describe a dilute nonvolatile solute in a volatile solvent. We depart from traditional practice only in that the mixture critical locus is considered input rather than output. However, from the coexistence properties of the solvent and the initial slopes of the mixture critical locus, the isothermal dew-bubble curves are predicted without any further adjustable parameters. The present result thus does not suffer from the need to correlate many parameters that has been experienced with the modified Leung-Griffiths model.

II. ASYMPTOTIC FORMULA FOR DEW-BUBBLE CURVES

Our starting point is the modified Leung-Griffiths model [2,6] which has yielded successful critical-region vapor-liquid equilibrium correlations for a wide variety of mixtures. On the coexistence surface, the independent variables of the model are ζ and t, where:

$$\zeta = e^{\mu_1/RT} \left/ \left(K e^{\mu_2/RT} + e^{\mu_1/RT} \right) \right. \tag{2}$$

and t is defined by Eq. (1) with a ζ-dependent T_c of the mixture [2]. Here μ_i is the chemical potential of fluid i, where i=1 for the nonvolatile solute and i=2 for the volatile solvent. Also, R is the gas constant and K is a temperature-dependent parameter that allows us, for monotonic $T_c(x)$, to impose the condition $\zeta = x_1$ on the critical locus [18].

We consider the small region of the phase diagram that describes a near-critical dilute nonvolatile solute in a volatile solvent.   Over a limited regime, the vapor pressure curve of the

solvent (solid line of Fig. 1) is approximately linear, with constant slope $(dP/dT)_\sigma$, and terminates at the solvent critical point C. The mixture critical locus CAD is assumed to be linear over this regime in P vs. x_1 and T vs. x_1 (and therefore in P vs. T), so dP_c/dx_1 and dT_c/dx_1 are constants. Our objective is to describe the isotherm AB, where A is a critical point of the mixture. Here BD is a locus of constant ζ, also linear over a limited regime, and according to the modified Leung-Griffiths model [2, 6], it is parallel to the vapor pressure curve, so $(dP/dT)_\zeta = (dP/dT)_\sigma$.

The validity of these assumptions depends on the mixture in question. The solvent vapor pressure curve may be expanded in powers of t:

$$P/T = P_c/T_c \left[1 + C_3(-t)^{1.9} + C_4 t + C_5 t^2 + ... \right] \tag{3}$$

so that beyond the linear term there are contributions of order $(-t)^{1.9}$ and t^2 with coefficients that can be fairly large. However, those two terms are nearly equal and opposite and largely cancel each other for small t. Therefore, vapor pressure curves of most pure fluids are very close to linear over the range $0.8\,P_c < P < P_c$.

Critical loci can assume many different shapes, and for some mixtures such as sulfur hexafluoride + propane [19] or benzene + methanol or 1-propanol [20], there is an abrupt hook at the critical point of the volatile fluid, so the present analysis does not apply. The initial part of the critical locus is more likely to be linear if the fluids are somewhat dissimilar. For example, critical loci for carbon dioxide + propane or n-butane have curvature and extrema along their initial intervals [21], but mixtures of carbon dioxide with alkanes from n-pentane to n-decane show sizeable linear intervals, although the critical locus becomes discontinuous at tridecane [22].

Elsewhere we have shown [23] that, along a line of constant ζ,

$$x_{11,v} = \zeta \pm C_1 |\alpha_2| (-t)^\beta + O(-t)^{2\beta} \tag{4}$$

where the plus refers to liquid and minus to vapor, C_1 is defined by Eq. (1), and

$$\alpha_2 = \lim_{t \to 0} \rho_c \left(x_l - x_v \right) / \left(\rho_l - \rho_v \right) \tag{5}$$

where α_2 is a measure of dew-bubble curve width. We have also shown that, in the dilute regime,

$$A = \frac{dP_c}{dx_1} - \left(\frac{dP}{dT} \right)_{\sigma, c} \frac{dT_c}{dx_1} \tag{6}$$

$$\alpha_2 = \left(RP_{c2} \, T_{c2} \right)^{-1} A x_1 \tag{7}$$

where A is the Krichevskii parameter [24] that has been shown to govern much of dilute critical-region thermodynamics [25]. A has dimensions of pressure, and in the case of Fig. 1, is negative.

We choose T as the temperature of the isotherm AB with critical composition $x_c(T)$ at point A, and Δx_{1c} as the difference in x_{1c} between points A and D, and treat both quantities as small. If P_J and T_J are the pressure and temperature at point J (A,B or D), then:

$$\Delta P = P_B - P_A = \left(P_D - P_A \right) - \left(P_D - P_B \right)$$

$$= \Delta x_{1c} \left[\frac{dP_c}{dx_1} - \left(\frac{\partial P}{\partial T} \right)_\zeta \frac{dT_c}{dx_1} \right] = A \, \Delta x_{1c} \tag{8}$$

$$t_B = \frac{T_A - T_D}{T_D} = \frac{-\Delta x_{1c} \left(\dfrac{dT_c}{dx_1} \right)}{T + \Delta x_{1c} \left(\dfrac{dT_c}{dx_1} \right)} = -\frac{\Delta x_{1c}}{T} \frac{dT_c}{dx_1} + \left(\Delta x_{1c} \right)^2 \tag{9}$$

We then use Eq. (4) along line DB with the assumption that C_1 (ζ) is approximately C_1 for the pure solvent, and $\zeta = x_{1c}$ (T) + Δx_1. Therefore, at point B, an arbitrary point on the isotherm of interest, and where Δ P and A are both negative,

$$x_{11,v} = x_{1c}(T) + \frac{\Delta P}{A} \pm C_1 \left(RP_{c2} \ T_{c2} \right)^{-1} \left[|A|x_{1c} (T) - \Delta P \right] \left(\frac{\Delta P}{AT} \ \frac{dT_c}{dx_1} \right)^{\beta} + .. \quad \textbf{(10)}$$

Equation (10) is our central result and is first used in Fig. 2. Several important observations can now be made:

1) At the "bird's beak" isotherm $T = T_{c2}$, the critical temperature of the solvent, x_{1c} (T) = 0. Thus on a P-x plot such as Fig. 2, both the dew and bubble curves have initial slope A, a result shown earlier by Levelt Sengers [26]. The difference $\Delta x_1 = x_{1\ell} - x_{1v}$ is proportional to $(-\Delta P)^{\beta+1}$ as noted by Harvey and Levelt Sengers [27]. Higher order terms would appear in Eq. (10), in addition to the terms explicitly omitted in our derivation, from a crossover theory. However, a simple scaling theory with an effective $\beta = 0.355$ has been shown to describe experiment over a fairly large range, so in considering the differences between a classical and a scaling law model, we will use the classical and effective exponents. Whether $\beta = 0.5$ or $\beta = 0.355$, the bubble curve on the bird's beak isotherm is initially convex upward and the dew curve concave upward, and the isotherm has an infinitely sharp point at the solvent critical point. For $T<T_{c2}$, the initial slopes of the bubble and dew curves differ according to a similar formula related to Henry's Law due to Japas and Levelt Sengers [28]:

$$\ln\left[(\partial\rho/\partial x)_B \ / \ (\partial\rho/\partial x)_D \right] = 2A \left(\rho_{\ell 2} - \rho_{c2} \right) / RT \ \rho_{c2}^2 \quad \textbf{(11)}$$

where B and D denote bubble and dew curves and $\rho_{\ell 2}$ is the solvent saturated liquid density, at temperature T.

2) Since there are terms in Eq. (10) proportional to $(-\Delta P)^{\beta}$ and $(-\Delta P)^{\beta+1}$, an earlier conclusion of Harvey and Levelt Sengers [27] is affirmed and made more precise. For fixed positive x_{1c} (T), at very small values of $|\Delta P|$ the term with the β exponent dominates. However, the coefficient of this term is proportional to x_{1c} (T), which in this regime is itself small, so there is a competition between the two terms. Also, rectilinear diameters of the dew-bubble curves are

straight lines of slope A.

3) Since nonclassical thermodynamic models are not yet as well developed for general purposes as classical equations of state, such classical equations are still commonly used even in the critical region. It is thus important to understand how significant the numerical errors will be from use of improper critical exponents. Such a question of course depends on the situation of interest, but Eq. (10) shows that, in the case of critical phase equilibrium of a dilute solution with nonvolatile solute, one can largely get away with the use of classical exponent values. There is not much difference between behavior governed initially by an exponent of 0.5 with transition to an exponent of 1.5, as compared with behavior governed initially by an exponent of 0.355 with transition to an exponent of 1.355.

The DECHEMA volume on vapor-liquid equilibrium [17] shows many examples of Peng-Robinson [4] correlations that are fairly good in the corner of the diagram that represents a dilute nonvolatile solute. The situation is quite different on the other side of the phase diagram for a dilute volatile fluid in a nonvolatile solvent and "pure-β behavior". There, the DECHEMA fits show many examples of convergence failures and deviation with experiment near critical conditions.

4) One of the problems with the modified Leung-Griffiths model is the proliferation of adjustable parameters. Equation (10), however, is a compact representation that depends only on solvent coexistence properties and the slopes of the critical line, without any free parameters.

5) Finally, we wish to comment on what we believe is a misunderstanding in the literature.   For any temperature such that $T_{c2} < T < T_{c1}$, and consequently for a finite nonzero x_{1c} (T), there is a term proportional to $(-\Delta P)^{\beta}$ in Eq. (10), and thus at the critical point of the dew-bubble isotherm,

$$\left(\partial P / \partial x\right)_{T}^{C, CXS} = 0 \tag{12}$$

However, Eq. (12) does not hold exactly at $T = T_{c2}$. For this bird's beak isotherm, the first term in brackets of Eq. (10) is zero, and the dew-bubble curve comes to an infinitely sharp point of slope A at the critical point of the solvent. Wichterle et al. [29], we believe incorrectly, asserted that Eq. (12) holds for the bird's beak isotherm also. Probably influenced by this analysis, Stryjek

et al. [30] of the same laboratory plotted the bird's beak isotherm for the nitrogen + methane mixture, in a closeup inset to their Fig. 6, as having a sharp hook so that the curves are horizontal at the critical point. There is insufficient data to support this conclusion, and in agreement with Levelt Sengers [26], we believe that conclusion to be incorrect. In other words, the bird's beak isotherm is like the beak of an egret, not like the beak of an ibis.

III. SIMPLE NONPOLAR MIXTURES

To test our result, we first examine some simple mixtures of nonpolar fluids. We seek mixtures with a number of isothermal dew-bubble curves at temperatures just above the critical temperature of the volatile component, and with a critical locus with a nearly linear initial segment. Kobayashi and co-workers have presented such experimental studies for methane + ethane [31], nitrogen + methane [30], and methane + propane [32]. These mixtures have also been correlated with the modified Leung-Griffiths model, so a comparison between that model, Eq. (10), and experiment can be made.

Figure 2 shows the comparison for methane + ethane. For each isotherm the solid line is Eq. (10), and the dotted line is the modified Leung-Griffiths model [2]. Except for minor parameter adjustments, this is equivalent to the fit of methane + ethane by Smith and Lynch [14]. The model was optimized to the constant-composition VLE data of Bloomer et al.[33].

Equation (10) and the full model are in agreement in the near-critical region, but diverge somewhat away from the critical locus. Both agree well with experimental data where they coincide, and Eq. (10) could be made to agree better with experiment by small shifts in the critical locus. That locus was optimized to the entire phase diagram, so a refitting of the initial linear segment of the critical locus could lead to improved agreement in Fig. 2, although there may also be small systematic discrepancies in the experimentally stated temperatures [26].

The derivation of Eq. (10) is a leading-order analysis of an expansion in t and x, and neglects many effects. Among these are the curvature of the solvent vapor pressure curve and loci of constant ζ, the curvature of the critical locus, the variation of critical density with composition, and other factors which are not understood fundamentally but are accounted for by adjustable parameters. Also, at points in the derivation higher powers of x_1 are neglected. However, for the supercritical region, here defined as the region above the critical pressure and temperature of nitrogen, and for temperatures at least up to the temperature at which $x_1 = 0.05$ on the critical locus

as well as at slightly lower pressures, Eq. (10) appears to be accurate.

The comparison for nitrogen + methane is shown in Figure 3. Except for the problem with the bird's beak isotherm noted earlier, the data of Stryjek, et al. [30] appear to be reliable. The Leung-Griffiths correlation of this mixture was presented earlier by Rainwater and Moldover [34] as an optimization to the data of Bloomer and Parent [35]. The overall pattern is similar to that of methane + ethane. Similar agreement is found on comparing to dilute solutions of propane in methane [32].

IV: CARBON DIOXIDE + COSOLVENT MIXTURES

In this section, we consider possible applications of Eq. 10 to problems in supercritical extraction. We first note that our equation is probably not applicable to the complex products usually extracted with pure supercritical carbon dioxide. The reason is that, as a separation process, supercritical extraction is advantageous only for solutes of very large molecules, and thus of substances that have a very high critical temperature (and probably decompose at that temperature). In general, mixtures of such substances with carbon dioxide do not have continuous critical loci. Our result may have some validity for discontinuous critical loci, but only over a very limited range.

We know approximately the conditions such that mixtures of a solute with carbon dioxide do not display discontinuous critical loci, from various studies of Lam and co-workers [21, 36]. For example, for the carbon dioxide + n-alkane family [21] that locus becomes discontinuous at tridecane (Tc = 676 K) and for the carbon dioxide + n-alkanol family [36], the discontinuity occurs at n-hexanol (Tc = 611 K). Critical temperature ratio is the most important (but not the only) determiner of whether a binary mixture critical locus is continuous, so we can presume carbon dioxide usually does not form mixtures of continuous critical loci with substances such that Tc > 600 K, and of molecules larger than those we have cited.

However, our expression was at first expected to be applicable to the thermodynamics of carbon dioxide + cosolvent mixtures used in supercritical extraction. Often a polar cosolvent, also called a modifier or entrainer, is used to enhance the solvation power or selectivity of the solvent. Typical choices of cosolvent are acetone, acetonitrile, and n-alkanols, and carbon dioxide mixtures with these substances (for n-alkanols up to n-hexanol [36]) are known or expected to possess continuous critical loci. There has been considerable recent interest in measuring VLE of carbon dioxide with these cosolvents in the region supercritical to carbon dioxide; in some cases the

experimental results are presented as unsmoothed three-dimensional surfaces [37, 38]. It would be useful to have an explicit mathematical expression for such surfaces, so it is useful to test Eq. (10) for such a purpose. We note that in previous studies of the Leung-Griffiths model [39], the presence of polarity leads to more parameters or larger values of parameters than otherwise but does not diminish the accuracy of the approach in correlation mode. We test the model here with the cosolvents acetone (T_c = 508 K) and ethanol (T_c = 514 K).

Figure 4 shows the comparison with our theoretical results and the isotherm at 313.15 K of Katayama et al. [40]. In contrast to the mixtures of the previous section, for this mixture there are no coexisting density data and no VLE data for acetone-rich mixtures so the Leung-Griffiths correlation is more speculative. Nevertheless, as optimized by simplex methods [41, 42], it agrees with the limited data quite well.

As shown, Eq. (10) for this isotherm follows the Leung-Griffiths model down about to the carbon dioxide critical pressure before diverging. We can improve the agreement with experiment significantly by adding a term $B \Delta P^2$ to Eq. 10, which gives curvature to the diameter, as shown in Fig. 4 with the choice $B = 0.009$ MPa^{-2}. This term also prevents, in this case, the unphysical result, possible from the original Eq. 10, that $x < 0$. Unfortunately, the phase boundary surface is no longer determined from the solvent properties and critical locus, in that adjustable parameter B, in general temperature-dependent, must be added. In this case, it is an inescapable conclusion from the data that the diameter is not linear. Nevertheless, Eq. (10) describes most of the properties of the isotherm.

Equation (10) provides a much poorer description of carbon dioxide + ethanol, as shown in Fig. 5. We have been unable to construct a successful Leung-Griffiths model for this mixture. Fig. 5 shows the experimental isotherms of Lim et al. [43] at 308.15 K and the predictions of Eq. (10).

One difficulty, as noted previously for carbon dioxide + methanol [10], is an inconsistency between VLE experiments and direct measurements of the critical locus. Figure 5 shows critical loci as optimized to that of Gurdial et al.[44] and as inferred from the data of Lim et al. [43]. These separate loci are in good agreement in P-x space, but not in P-T space. The isotherm determined from Eq. 10 and the former critical locus has a critical point inconsistent with the VLE data and is

extremely narrow compared with experiment. Here the slopes dP/dT of the solvent vapor pressure

curve and the critical locus are quite close, so there is a large sensitivity of Eq. 10 to variations in the critical locus.

The isotherm determined from Eq. 10 and the latter critical locus is much wider than the first theoretical curve, but still much narrower than the experimental curve. Previous studies [16,23] have shown that the "amplitude" of the phase boundary curves are closely related to the properties of the solvent vapor pressure curve and critical locus while the diameters may not be, but in this case the theory breaks down for the amplitudes as well. There is some clear scatter in the data on the vapor side, and the smoothed data might be described with the mathematical form of Eq. 10 with a quadratic term, but with coefficients that would be adjustable parameters. We can only speculate on the apparent failure of our approach for this mixture. While carbon dioxide + ethanol is generally regarded to be Type 1 in the nomenclature of Van Konynenburg and Scott [46] (Class 1^P in the recently proposed nomenclature of Bolz et al.[47], it may be near P a transition to Type 5 of Van Konynenburg and Scott (Class 2^P of Bolz et al.). In this transition, the critical locus changes from continuous to a locus broken by a three-phase, liquid-liquid-vapor locus. Proximity to such a transition may introduce a different type of fluctuation, the predominantly composition flucuations of liquid-liquid equilibrium in addition to the predominantly density fluctuations of vapor-liquid equilibrium, and the assumptions of the theory may break down. To resolve this issue, further investigation is needed, perhaps in conjunction with classical equations of state which work somewhat better in this regime for the present mixture.

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FIGURE CAPTIONS

Figure 1. Schematic pressure-temperature diagram of a near-critical dilute solution, linearized. Solid line, vapor pressure locus of solvent; dotted line; critical locus; broken line, isotherm; dashed line, locus of constant zeta.

Figure 2. Pressure-composition diagram for dilute ethane in methane. Experimental data and temperatures as indicated. Critical locus, broken line; solid lines, asymptotic formula; dotted lines; Leung-Griffiths model; dashed lines, diameters of isotherms.

Figure 3. Pressure-composition diagram for dilute methane in nitrogen. Experimental data and temperatures as indicated. Linetypes same as Fig. 2.

Figure 4. Pressure-composition diagram for dilute acetone in carbon dioxide. Experimental data, inverted triangles (Ref. 40, 313.15 K). Linetypes same as Fig 2. except solid line, original asymptotic formula and diameter; dashed line, modified asymptotic formula and diameter with quadratic term in diameter.

Figure 5. Pressure-composition diagram for dilute ethanol in carbon dioxide. Experimental critical points, empty circles Ref. 44, empty triangles Ref. 45. Filled circles, VLE data at 308.15 K. Broken line, critical locus optimized to measured critical points, with critical point C1 at 308.15 K. Dotted line, critical locus optimized to VLE, with critical point C2 at 308.15 K. Solid lines, respective asymptotic formula results; dashed lines, respective diameters.